

# Exploitation of the Second Law: Coleman–Noll and Liu Procedure in Comparison

Vita Triani<sup>1,\*</sup>, Christina Papenfuss<sup>2</sup>, Vito A. Cimmelli<sup>3</sup>, and Wolfgang Muschik<sup>4</sup>

<sup>1</sup>Institut für Theoretische Physik, Technische Universität Berlin, on leave from: Department of Mathematics and Computer Science, University of Basilicata, Campus Macchia Romana, I-85100 Potenza, Italy

<sup>2</sup>Institut für Mechanik and Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin, Germany

<sup>3</sup>Department of Mathematics and Computer Science, University of Basilicata, Campus Macchia Romana, I-85100 Potenza, Italy

<sup>4</sup>Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin, Germany

\*Corresponding author (vitrian@virgilio.it)

## Abstract

A comparison is made between two classical methods for the exploitation of the second law of thermodynamics: the Coleman–Noll and the Liu procedure. On the example of a rigid heat conductor with general entropy flux, it is shown that the two procedures are equivalent. This equivalence is demonstrated in the case of a state space including the wanted fields, only, as well as in the case of gradients being relevant for constitutive equations, too. Also, the possible importance of an internal variable or an internal degree of freedom is considered.

## 1. Introduction

In continuum thermodynamics, the entropy principle constitutes a basic tool in deriving thermodynamic restrictions on constitutive equations. In fact, the requirement of the Coleman–Mizel formulation of the second law [1] that all solutions of the balance equations have to satisfy the dissipation inequality greatly reduces the freedom in modelling the material behavior [2–4].

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Exploitation of the second law rests upon the local balance of entropy

$$\sigma_s = \dot{s} + \operatorname{div} \mathbf{J}_s - r_s \geq 0, \quad (1)$$

where  $s$  means the entropy density,  $\mathbf{J}_s$  is the entropy flux vector,  $r_s$  is the entropy supply density, and  $\sigma_s$  means the local entropy production. Here and in the following, we have assumed the material to be at rest,  $\mathbf{v} \equiv \mathbf{0}$ . In this case, the material time derivative  $\dot{s}$  and the partial time derivative  $\partial s / \partial t$  are equal. The second law of thermodynamics forces  $\sigma_s$  to be non-negative.

The local balance of internal energy for a material at rest reads

$$\dot{\varepsilon} + \operatorname{div} \mathbf{q} - r = 0, \quad (2)$$

where  $\varepsilon$  is the internal energy density,  $\mathbf{q}$  is the heat flux vector, and  $r$  is the heat supply density. Originally, in rational thermodynamics [5], the vector  $\mathbf{J}_s$  and the entropy supply  $r_s$  are assumed to be given by

$$\mathbf{J}_s = \frac{\mathbf{q}}{\vartheta}, \quad (3)$$

$$r_s = \frac{r}{\vartheta}. \quad (4)$$

Here  $\vartheta$  is the absolute temperature. However, it is known that for instance in the case of mixtures of chemical components [6], or in the case of liquid crystals [7], this constitutive assumption on the entropy flux is too restrictive. In our exploitation of the dissipation inequality, we will not make any assumption about the entropy flux, which is considered as an independent constitutive quantity, as it is done in some branches of rational thermodynamics [8, 9]; see also [10].

Once the local balance of energy (2) is taken into account, then Eq. (1), (3), and (4) yield

$$-(\dot{\psi} + s\dot{\vartheta}) - \frac{1}{\vartheta} \mathbf{q} \cdot \operatorname{grad} \vartheta \geq 0, \quad (5)$$

with the Helmholtz free energy  $\psi$  defined by

$$\psi := \varepsilon - \vartheta s. \quad (6)$$

The unilateral differential relation (5) is referred to as Clausius–Duhem inequality [5].

There are two different techniques, well known in the literature, for the exploitation of the second law: the Coleman–Noll procedure [11] and the Liu

procedure [12]. Both are faced with the problem of finding necessary and sufficient conditions satisfying Eq. (1) under the differential constraint of the energy balance (2), and, depending on the problem, of other additional balances as well. For examples of the application of the Coleman–Noll method, see, e.g., [13], and for the Liu–procedure see e.g., [8, 14]. However, several remarkable differences distinguish the two approaches. In the original version of rational thermodynamics, Coleman and Noll assume that Eqs. (3) and (4) hold, and take into account the constraint (2) by considering Eq. (5) instead of Eq. (1). In other words, the constraints are **substituted** into the inequality to be solved. Here we define the methods to be compared in such a way that the entropy flux is an undetermined constitutive quantity, and the Coleman–Noll technique means that all balance equations, and eventually other differential equations for additional variables, are inserted into the expression for the entropy production.

In the Liu technique, Eqs. (3) and (4) are not assumed while the constraint (2), multiplied by an undetermined Lagrange multiplier, is **added** to Eq. (1). In general, each constraint is taken into account, introducing a new (undetermined) multiplier. Then, a classical result by Farkas and Minkowski [15, 16] is applied (see also [4]), which gives necessary and sufficient conditions for a linear inequality on a finite dimensional space to be implied by a given set of linear equalities.

In this paper, we present three different classes of state spaces for which the Coleman–Noll technique and the Liu technique are equivalent for a rigid heat conductor. In two cases, the chosen constitutive state spaces contain gradients of the wanted fields. We do not use the constitutive assumption (3), but we take into account Eqs. (1), (2) and (4).

In Section 2, we obtain two inequalities generated by applying the Coleman–Noll and the Liu procedure, respectively, to Eqs. (1) and (2). We prove that these inequalities are equivalent in the sense that they result in the same thermodynamic restrictions for the constitutive equations. In particular, the reduced entropy inequality, which represents the local entropy production  $\sigma_s$ , is the same in both cases, as well as the constraints on constitutive functions.

In Section 3, we consider a weakly non-local constitutive space including the first gradient of the basic fields. Again, both the derived reduced inequalities are equivalent.

As an example, in Section 4, we consider a weakly non-local state space of a rigid heat conductor with internal variables. Such a case has already been treated in the framework of a thermodynamic approach to the problem of

boundary conditions in the presence of internal variables [17]. Also in this case, the thermodynamic restrictions are equivalent.

Finally, in Section 5, we provide a sketch of our main conclusions and discuss some possible generalizations of the present results.

## 2. A state space without derivatives

Let us consider a rigid heat conductor whose constitutive state space is spanned by the specific internal energy  $\varepsilon$  and by vector fields  $\mathbf{z}$ ,

$$\mathbf{Z} = (\varepsilon, \mathbf{z}), \quad (7)$$

not containing derivatives of the internal energy. The set of governing equations for  $\mathbf{z}$  is in balance form,

$$\dot{\mathbf{z}} + \text{div } \Phi = \pi. \quad (8)$$

Here,  $\Phi$  is the flux of  $\mathbf{z}$  and  $\pi$  its production. It is worth noticing that the system we are dealing with encompasses the 4-field model of extended thermodynamics [9, 18], which can be obtained by Eqs. (2) and (8) and by identifying  $\mathbf{z} \doteq \mathbf{q}$  in the case that is considered here. The constitutive quantities  $s$ ,  $\mathbf{J}_s$ ,  $\mathbf{q}$ , and  $\Phi$  are assumed to depend on the chosen state space  $(\varepsilon, \mathbf{z})$ .

### 2.1. Coleman–Noll method

By **substituting** the values of  $\dot{\varepsilon}$  and  $\dot{\mathbf{z}}$ , given by Eqs. (2) and (8), into the time derivative of  $s$  in Eq. (1), we obtain the Coleman–Noll inequality (CNI):

$$\begin{aligned} \left( -\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \varepsilon} + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \left( -\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} + \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} + \\ + \frac{\partial s}{\partial \mathbf{z}} \cdot \pi + \frac{\partial s}{\partial \varepsilon} r - r_s \geq 0. \quad (9) \end{aligned}$$

We now assume that the entropy supply is given by Eq. (4). However, we do not presuppose that the entropy flux is  $\mathbf{q}/\vartheta$ , since this form seems to hold only for a restricted class of materials. Different proposals for a generalized entropy flux are given in [6, 8, 19, 20], and in the context of extended thermodynamics; see [18]. Under the previous assumptions and due to the thermodynamic relation  $\partial s / \partial \varepsilon := 1/\vartheta$ , the supply terms in the inequality (9) cancel, and we

obtain

$$\begin{aligned} & \left( -\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \varepsilon} + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \\ & + \left( -\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} + \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} + \frac{\partial s}{\partial \mathbf{z}} \cdot \boldsymbol{\pi} \geq 0. \quad (10) \end{aligned}$$

## 2.2. Liu method

The Liu inequality can be obtained by multiplying Eq. (2) by an a priori undetermined scalar Lagrange–Farkas multiplier  $-\lambda(\varepsilon, \mathbf{z})$ , Eq. (8), by a vectorial Lagrange–Farkas multiplier  $-\boldsymbol{\lambda}(\varepsilon, \mathbf{z})$  and **adding** the obtained equations to Eq. (1). Then we obtain the Liu inequality (LI),

$$\begin{aligned} & \left( \frac{\partial s}{\partial \varepsilon} - \lambda \right) \dot{\varepsilon} + \left( -\lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \varepsilon} + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \left( \frac{\partial s}{\partial \mathbf{z}} - \boldsymbol{\lambda} \right) \cdot \dot{\mathbf{z}} + \\ & + \left( -\lambda \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} + \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} + \boldsymbol{\lambda} \cdot \boldsymbol{\pi}(\mathbf{z}) \geq 0. \quad (11) \end{aligned}$$

As a consequence of the Liu–Farkas lemma [12, 15, 16, 21], the higher derivatives in the brackets in Eq. (11) are treated as independent variables. The inequality implies that the brackets vanish, and we have

$$\lambda = \frac{\partial s}{\partial \varepsilon}, \quad \boldsymbol{\lambda} = \frac{\partial s}{\partial \mathbf{z}}, \quad (12)$$

$$-\lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \varepsilon} + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} = \mathbf{0}, \quad (13)$$

$$-\lambda \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} + \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} = \mathbf{0}, \quad (14)$$

$$\boldsymbol{\lambda} \cdot \boldsymbol{\pi} \geq 0. \quad (15)$$

The same set of equations is obtained from an exploitation of the entropy inequality together with the balance equations, applying the Coleman–Mizel formulation of the second law; for a proof, see [4].

If instead we require that the fields  $\varepsilon$  and  $\mathbf{z}$  satisfy the CNI (10), since for the higher derivatives  $\nabla \varepsilon$  and  $\nabla \mathbf{z}$  arbitrary values can be prescribed (see, e.g., [22]

for details), we obtain

$$-\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \varepsilon} + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} = \mathbf{0}, \quad (16)$$

$$-\frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} + \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} = \mathbf{0}, \quad (17)$$

$$\frac{\partial s}{\partial \mathbf{z}} \cdot \boldsymbol{\pi} \geq 0. \quad (18)$$

It is easily seen that, if Eqs. (12)–(15) hold, then we can substitute Eq. (12) into Eqs. (13)–(15), in order to obtain Eqs. (16)–(18). Conversely, if Eqs. (16)–(18) hold, then Eqs. (12)–(15) are recovered by setting  $\lambda \doteq \frac{\partial s}{\partial \varepsilon}$  and  $\boldsymbol{\lambda} \doteq \frac{\partial s}{\partial \mathbf{z}}$ . In such a way we have proved the following:

### Theorem of equivalence

*If the state space (7) is chosen and if the evolution of  $(\varepsilon, \mathbf{z})$  is governed by the system (2) and (8), then the CNI (10) and the LI (11) are equivalent and result in the same set of thermodynamic restrictions.*

### 3. Equivalence of CNI and LI in the case of gradient theory

In this section, we assume that the thermodynamic state space is spanned by the set of variables

$$\mathbf{Z} = \{\varepsilon, \mathbf{z}, \nabla \varepsilon, \nabla \mathbf{z}\}, \quad (19)$$

namely a first-order non-locality enters the constitutive equations. Moreover, let the evolution of the basic field  $(\varepsilon, \mathbf{z})$  be governed by Eqs. (2) and (8). If  $\mathbf{z}$  is an internal variable of state, the model leads to some celebrated equations of low-temperature physics such as the Ginsburg–Landau and Guyer–Krumhansl equation [23].

Using Eqs. (1), (2), and (8), we can apply the CN technique and write the entropy production  $\sigma_s$  as follows:

$$\begin{aligned} \sigma_s = & \frac{\partial s}{\partial \mathbf{z}} \cdot \boldsymbol{\pi} + \frac{\partial s}{\partial \nabla \varepsilon} \cdot \nabla \dot{\varepsilon} + \frac{\partial s}{\partial \nabla \mathbf{z}} : \nabla \dot{\mathbf{z}} + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \\ & + \left( \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} + \left( \frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \nabla \varepsilon} \right) : \nabla^2 \varepsilon + \\ & + \left( \frac{\partial \mathbf{J}_s}{\partial \nabla \mathbf{z}} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \nabla \mathbf{z}} \right) : \nabla^2 \mathbf{z} \geq 0. \end{aligned} \quad (20)$$

By the same arguments as in the previous section, it follows that Eq. (20) is fulfilled for any solution of the balance equations, if and only if

$$s = s(\varepsilon, \mathbf{z}), \quad (21)$$

$$\begin{aligned} \frac{\partial s}{\partial \mathbf{z}} \cdot \boldsymbol{\pi} + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \\ + \left( \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} \geq 0, \end{aligned} \quad (22)$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \nabla \varepsilon} = \mathbf{0}, \quad (23)$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \mathbf{z}} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \mathbf{z}} - \frac{\partial s}{\partial \mathbf{z}} \cdot \frac{\partial \Phi}{\partial \nabla \mathbf{z}} = \mathbf{0}. \quad (24)$$

On the other hand, by applying the Liu procedure, the entropy production takes the form

$$\begin{aligned} \sigma_s = \left[ \frac{\partial s}{\partial \varepsilon} - \lambda \right] \dot{\varepsilon} + \left[ \frac{\partial s}{\partial \mathbf{z}} - \boldsymbol{\lambda} \right] \cdot \dot{\mathbf{z}} + \frac{\partial s}{\partial \nabla \varepsilon} \cdot \nabla \dot{\varepsilon} + \frac{\partial s}{\partial \nabla \mathbf{z}} : \nabla \dot{\mathbf{z}} + \\ + \left[ \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \varepsilon} \right] \cdot \nabla \varepsilon + \left[ \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} - \lambda \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \mathbf{z}} \right] : \nabla \mathbf{z} + \\ + \left[ \frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \nabla \varepsilon} \right] : \nabla^2 \varepsilon + \left[ \frac{\partial \mathbf{J}_s}{\partial \nabla \mathbf{z}} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \mathbf{z}} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \nabla \mathbf{z}} \right] : \nabla^2 \mathbf{z} + \\ + \boldsymbol{\lambda} \cdot \boldsymbol{\pi} \geq 0. \end{aligned} \quad (25)$$

The inequality above implies the thermodynamic restrictions

$$\lambda = \frac{\partial s}{\partial \varepsilon}, \quad \boldsymbol{\lambda} = \frac{\partial s}{\partial \mathbf{z}}, \quad (26)$$

$$s = s(\varepsilon, \mathbf{z}), \quad (27)$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \nabla \varepsilon} = \mathbf{0}, \quad (28)$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \mathbf{z}} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \mathbf{z}} - \boldsymbol{\lambda} \cdot \frac{\partial \Phi}{\partial \nabla \mathbf{z}} = \mathbf{0}, \quad (29)$$

$$\begin{aligned}
& \lambda \cdot \pi + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} - \lambda \frac{\partial \Phi}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \\
& + \left( \frac{\partial \mathbf{J}_s}{\partial \mathbf{z}} - \lambda \cdot \frac{\partial \mathbf{q}}{\partial \mathbf{z}} - \lambda \cdot \frac{\partial \Phi}{\partial \mathbf{z}} \right) : \nabla \mathbf{z} \geq 0.
\end{aligned} \tag{30}$$

Again, we can see that if Eqs. (26)–(30) hold, then on substituting Eq. (26) into Eqs. (28)–(30) we get the thermodynamic restrictions (21)–(24). Conversely, if Eqs. (21)–(24) are true, we can recover Eqs. (26)–(30) by setting  $\lambda \doteq \frac{\partial s}{\partial \varepsilon}$  and  $\lambda \doteq \frac{\partial s}{\partial \mathbf{z}}$ . Hence, we conclude that the equivalence theorem proved in Section 2 can be extended to the state space (19) of a first-order gradient theory. Moreover, it is easily seen that the considerations above apply to a gradient theory of arbitrary order.

#### 4. A gradient theory with an internal variable

The internal variables of state constitute an efficient means of dealing with non-equilibrium processes involving complex thermodynamical systems [24]. This is the case, for instance, in the inelastic behavior of solids or in the relaxation effects in thermo-viscous fluids [25]. Their evolution is ruled either by ordinary differential equations (local theory) [26], or by partial differential equations (weakly non-local theory) [16, 23, 27–30]. In this last case, exploitation of second law takes on a particular meaning, since it also allows the derivation of suitable boundary conditions [17].

In the present section, we are dealing with a rigid heat conductor with a single internal variable. We assume that the material is described by the following choice of the state space:

$$\mathbf{Z} = \{\varepsilon, \nabla \varepsilon, \alpha, \nabla \alpha\}, \tag{31}$$

where  $\alpha$  is a scalar internal variable satisfying the partial differential equation

$$\dot{\alpha} = f(\alpha, \nabla \alpha), \tag{32}$$

from which follows the extended evolution equation for  $\nabla \alpha$ ,

$$\nabla \dot{\alpha} = \frac{\partial f}{\partial \alpha} \nabla \alpha + \frac{\partial f}{\partial \nabla \alpha} \cdot \nabla^2 \alpha. \tag{33}$$

Equations (32) and (33) together with the local balance of the energy (2) are the field equations for the wanted fields  $\varepsilon$  and  $\alpha$ . Let us remark that the argument of  $f$  is now included in  $\mathbf{Z}$ , meaning that  $\dot{\alpha}$  is expressed as a function



of the elements of the state space variables. Such a situation is rather different from that of the previous section in which  $\mathbf{z}$  can also be an internal degree of freedom, due to a complex structure of the material. However, because of Eq. (8),  $\dot{\mathbf{z}}$  cannot be expressed as a function of the state space, due to the flux term in the equation for  $\mathbf{z}$ . In other words, the right-hand side of Eq. (32) does not contain the higher derivatives of the basic field. This case is very frequent in the theory of complex materials in which the internal parameters are often governed by ordinary differential equations. In such a case, if only the evolution equation is substituted into the entropy inequality, some information is lost and one can get only an additional term in the reduced entropy inequality representing the local entropy production due to the internal variable. To overcome this problem, we substitute into the entropy inequality the extended evolution equation, too, in such a way that the obtained inequality contains derivatives of  $\alpha$  of higher order than those already included in the state space [16,23,28–30]. It is easily seen by direct inspection that the further substitution of the second-order extended evolution equation, too, does not furnish any additional constitutive restriction.

The Coleman–Noll technique is applied by substituting Eq. (33) into the entropy inequality. In such a case, due to Eqs. (32), (33), and (2), the CNI reads

$$\begin{aligned} \sigma_s = & \frac{\partial s}{\partial \alpha} f + \left( \frac{\partial s}{\partial \nabla \alpha} \frac{\partial f}{\partial \alpha} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \alpha} + \frac{\partial \mathbf{J}_s}{\partial \alpha} \right) \cdot \nabla \alpha + \\ & + \left( \frac{\partial s}{\partial \nabla \alpha} \frac{\partial f}{\partial \nabla \alpha} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \alpha} + \frac{\partial \mathbf{J}_s}{\partial \nabla \alpha} \right) : \nabla^2 \alpha + \frac{\partial s}{\partial \nabla \varepsilon} \cdot \nabla \dot{\varepsilon} + \\ & + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \left( \frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} \right) : \nabla^2 \varepsilon \geq 0. \end{aligned} \quad (34)$$

Again, by the same arguments as in the previous sections, we obtain the thermodynamic restrictions

$$s = s(\alpha, \nabla \alpha, \varepsilon), \quad (35)$$

$$\frac{\partial s}{\partial \nabla \alpha} \frac{\partial f}{\partial \nabla \alpha} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \alpha} + \frac{\partial \mathbf{J}_s}{\partial \nabla \alpha} = \mathbf{0}, \quad (36)$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} = \mathbf{0}, \quad (37)$$

together with the reduced entropy inequality

$$\frac{\partial s}{\partial \alpha} f + \left( \frac{\partial s}{\partial \nabla \alpha} \frac{\partial f}{\partial \alpha} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \alpha} + \frac{\partial \mathbf{J}_s}{\partial \alpha} \right) \cdot \nabla \alpha + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \frac{\partial s}{\partial \varepsilon} \frac{\partial \mathbf{q}}{\partial \varepsilon} \right) \cdot \nabla \varepsilon \geq 0. \quad (38)$$

On the other hand, due to Eqs. (32), (33), and (2), the Liu technique results in the inequality

$$\begin{aligned}
 \sigma_s = & \frac{\partial s}{\partial \alpha} \dot{\alpha} + \frac{\partial s}{\partial \nabla \alpha} \cdot \nabla \dot{\alpha} + \frac{\partial s}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial s}{\partial \nabla \varepsilon} \cdot \nabla \dot{\varepsilon} + \\
 & + \frac{\partial \mathbf{J}_s}{\partial \alpha} \cdot \nabla \alpha + \frac{\partial \mathbf{J}_s}{\partial \nabla \alpha} \cdot \nabla^2 \alpha + \frac{\partial \mathbf{J}_s}{\partial \varepsilon} \cdot \nabla \varepsilon + \frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} : \nabla^2 \varepsilon - \lambda_a (\dot{\alpha} - f) - \\
 & - \lambda \left( \dot{\varepsilon} + \frac{\partial \mathbf{q}}{\partial \alpha} \cdot \nabla \alpha + \frac{\partial \mathbf{q}}{\partial \varepsilon} \cdot \nabla \varepsilon + \frac{\partial \mathbf{q}}{\partial \nabla \alpha} : \nabla^2 \alpha + \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} : \nabla^2 \varepsilon \right) - \\
 & - \lambda \cdot \left( \nabla \dot{\alpha} - \frac{\partial f}{\partial \alpha} \nabla \alpha - \frac{\partial f}{\partial \nabla \alpha} \cdot \nabla^2 \alpha \right) \geq 0.
 \end{aligned} \tag{39}$$

The inequality above can be rearranged as follows:

$$\begin{aligned}
 \sigma_s = & \left( \frac{\partial s}{\partial \varepsilon} - \lambda \right) \dot{\varepsilon} + \left( \frac{\partial s}{\partial \nabla \alpha} - \boldsymbol{\lambda} \right) \cdot \nabla \dot{\alpha} + \left( \frac{\partial s}{\partial \alpha} - \lambda_a \right) \dot{\alpha} + \frac{\partial s}{\partial \nabla \varepsilon} \cdot \nabla \dot{\varepsilon} + \\
 & + \left( \frac{\partial \mathbf{J}_s}{\partial \alpha} - \lambda \frac{\partial \mathbf{q}}{\partial \alpha} + \frac{\partial f}{\partial \alpha} \boldsymbol{\lambda} \right) \cdot \nabla \alpha + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} \right) \cdot \nabla \varepsilon + \\
 & + \left( \frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} \right) : \nabla^2 \varepsilon + \\
 & + \left( \frac{\partial \mathbf{J}_s}{\partial \nabla \alpha} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \alpha} + \frac{\partial f}{\partial \nabla \alpha} \boldsymbol{\lambda} \right) : \nabla^2 \alpha + \lambda_a f \geq 0.
 \end{aligned} \tag{40}$$

By applying the Liu–Farkas lemma [12,21] to Eq. (40), we get the following thermodynamic restrictions:

$$\lambda = \frac{\partial s}{\partial \varepsilon}, \quad \boldsymbol{\lambda} = \frac{\partial s}{\partial \nabla \alpha}, \quad \lambda_a = \frac{\partial s}{\partial \alpha}, \tag{41}$$

$$s = s(\alpha, \nabla \alpha, \varepsilon), \tag{42}$$

$$\boldsymbol{\lambda} \frac{\partial f}{\partial \nabla \alpha} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \alpha} + \frac{\partial \mathbf{J}_s}{\partial \nabla \alpha} = \mathbf{0}, \tag{43}$$

$$\frac{\partial \mathbf{J}_s}{\partial \nabla \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \nabla \varepsilon} = \mathbf{0}, \tag{44}$$

$$\begin{aligned}
 \Lambda_a f + & \left( \boldsymbol{\lambda} \frac{\partial f}{\partial \alpha} - \lambda \frac{\partial \mathbf{q}}{\partial \alpha} + \frac{\partial \mathbf{J}_s}{\partial \alpha} \right) \cdot \nabla \alpha + \\
 & + \left( \frac{\partial \mathbf{J}_s}{\partial \varepsilon} - \lambda \frac{\partial \mathbf{q}}{\partial \varepsilon} \right) \cdot \nabla \varepsilon \geq 0.
 \end{aligned} \tag{45}$$

Let us assume that Eqs. (41)–(45) hold. Then we can substitute Eq. (41) into the remaining relations and obtain Eqs. (35)–(38). Vice versa, if Eqs. (35)–(38) hold, then the Liu relations Eqs. (41)–(45) are recovered, if we set  $\lambda \doteq \frac{\partial s}{\partial \varepsilon}$  and  $\lambda \doteq \frac{\partial s}{\partial \nabla \alpha}$ . This proves that, also in this case, the CN and Liu procedures have the same consequences on the constitutive equations.

## 5. Conclusions

In this paper, we have compared the celebrated Coleman–Noll and Liu techniques exploiting the second law for the example of a rigid heat conductor. We have seen that the Coleman–Noll procedure, although it has been originally designed for the class of materials for which  $\mathbf{J}_s = \frac{\mathbf{q}}{\vartheta}$ , can be applied, if the entropy flux is assumed to be an open constitutive equation. Consequently, it can be used also for complex materials. By the substitution technique developed by Coleman and Noll [11], we obtained the local form of entropy production  $\sigma_s$  in various situations. We also get the local entropy production by using the procedure of the Lagrange multipliers developed by Liu [12]. We have analyzed the local and the weakly non-local theory, and in both cases we have proved that the two expressions of  $\sigma_s$  are equivalent in the case of a rigid heat conductor. As a simple but meaningful application, we have considered a gradient theory of a rigid heat conductor with a scalar internal variable. Also in this case, we proved the complete equivalence of the Coleman–Noll and Liu techniques.

An interesting result is that the entropy density (27) does not depend on the highest variables of the state space (19), if Eq. (8) is valid. If the evolution equations are of relaxation type (32), the entropy density (42) depends also on the highest derivatives of the state space (31).

Let us ask which procedure might be technically easier. To our opinion, the Coleman–Noll procedure is less cumbersome in general, and so it is convenient to apply such a technique in dealing with complex materials, whose constitutive space contains several tensorial thermodynamical variables. On the other hand, this procedure can be applied in different ways, leading to different results, whose comparison is, in general, not easy.

On the contrary, the Liu procedure is clear and uniquely defined, whatever the system of governing equations is, and such a property uniquely determines the set of the thermodynamical restrictions. Hence, when the thermodynamical state space is not too complex, the application of this procedure would be preferable.

The case of a rigid heat conductor considered here is not the general one, which may be represented by a deformable body whose constitutive equations contain space and time derivatives of the basic variables up to an arbitrary order and by the presence of extra variables, such as the deformation tensor, the symmetric part of the velocity gradient, the plasticity tensor, and which also include different types of time derivatives. We presume that also in this more general case the equivalence should not be affected, although the proof of this conjecture may be cumbersome.

But there are situations in which the equivalence of both procedures cannot be expected: If in case of the state space spanned by the variables  $\mathbf{Z} = (\varepsilon, \mathbf{z})$ , the governing differential equation for the higher derivative  $\dot{\mathbf{z}}$  cannot be resolved to  $\dot{\mathbf{z}}$ , so that they cannot be inserted into the dissipation inequality (1), in contrast to Eq. (8), which is in a normal form. Here the Coleman–Noll procedure fails, but the Liu procedure is still possible by taking the governing differential equations as constraints into consideration according to Eq. (11).

Another point of future research is how the results generated by the Coleman–Noll and Liu procedures are altered, if some of the governing equations are not taken into account as constraints, or if differentiated balance equations are treated as additional constraints. What happens with both the procedures if the well-posedness of the Cauchy problem is not warranted, if stochastic variables are included in the state space, or if transitions to the chaotic regime appear?

These short remarks demonstrate that the systematic exploitation of the dissipation inequality makes more investigations necessary.

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